

Osmium isotope and PGE reference materials OKUM and MUH-1

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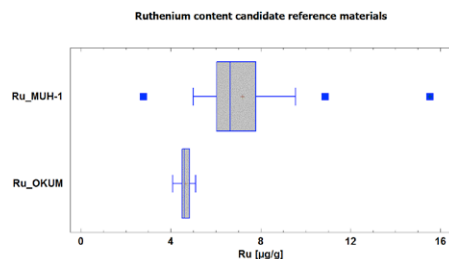
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As for many isotope systems, certified reference materials (CRM) of *real* samples are very sparse. Solutions with known isotopic composition exist for QA/QC purposes, but for the evaluation of the combined standard measurement uncertainty *matrix matched* CRM need to be applied. For method validation, calibration and verification purposes of Os isotopic composition and platinum group element content (PGE) two ultramafic RM with different matrices have been prepared. OKUM, an ultramafic komatiite and MUH-1, a depleted harzburgite (Kraubath, Austria) have been prepared and are already certified for major and trace elements by an interlaboratory certification process lead by the International Association of Geoanalysts (IAG). Whereas the dominant PGE bearing phases in lherzolites are sulfides, the dominant phases in harzburgites are alloys and laurites. As a result, the homogeneity of harzburgites with respect to PGE distribution is generally much worse than for lherzolites and komatiites.

Initial homogeneity tests with 2 g and smaller test portion sizes demonstrate this significant difference.



This test already demonstrates that validated methods with lherzolithic RM such as UB-N cannot be applied to harzburgites as these are generally heterogeneous.

Both RM show PGE distributions typical for mantle restites and komatiite melts with ¹⁸⁷Os/¹⁸⁸Os of 0.127 and 0.27 respectively and thus ideal matrix RM for mantle studies.

Early diagenetic quartz formation at a deep iron oxidation front in the Eastern Equatorial Pacific

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Diagenetic quartz formation at low temperature is still not well understood. Lithified chert consisting of microcrystalline quartz was recovered at ODP Site 1226 in the Eastern Equatorial Pacific [1] near the base of a 420 m thick Miocene-Holocene sequence of nanofossil and diatom ooze. Precipitation temperatures calculated from oxygen isotope values in the cherts are near to present porewater temperatures, and a sharp depletion in dissolved silica occurs at 385 m, indicating that silica precipitation is still going on.

It has been observed that quartz forms in experiments in the presence of fresh precipitated iron oxyhydroxides [2]. Indeed, a deep iron oxidation front occurs above 400 m sediment depth, which is caused by upward diffusing nitrate from an oxic seawater aquifer in the underlying basaltic crust. Sequential iron extraction and analysis of the X-ray absorption near-edge structure (XANES) revealed that iron in the cherts predominantly occurs as illite and amorphous iron oxide, whereas iron in the nanofossil and diatom ooze occurs mainly in smectites. Mössbauer spectroscopy confirmed that the amorphous iron in the cherts is largely oxidized.

Two possible mechanisms may be operative during early diagenetic chert formation at iron oxidation fronts: (1) quartz precipitation may be initiated by adsorption of silica to freshly precipitated iron oxides. (2) Iron oxidation lowers the pH, which brings the reactive surfaces of iron oxides closer to the zero point of charge, facilitating the binding of SiO₂. We suggest that the formation of early-diagenetic chert at iron oxidation fronts is an important process in suboxic zones of silica-rich sediments. The largest iron oxidation front ever occurred during the great oxidation event ca. 2.5 Ga ago, when large amounts of iron and chert beds were deposited.

[1] D'Hondt *et al.* (2002) *Proc. ODP, Init. Repts.* **201**. [2] Harder & Flehmig (1970) *Geochim. Cosmochim. Acta* **34**, 295-305.